Very Large Pi-Conjugation Despite Strong Non-Planarity: a Path for Designing New Semiconducting Polymers

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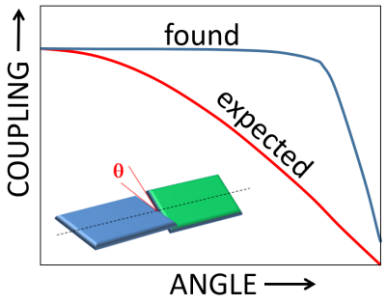
Abstract

When two pi-conjugated fragments are connected by a bond between two sp2 carbon atoms, a torsion around this bond is expected to break the overall pi-conjugation. We show that for specially selected monomers the pi-conjugation is insensitive to torsions around a C-C bonds up to about 60 degrees. We provide a number of examples for this very unexpected phenomenon and a simple explanation. We propose that this feature can be incorporated into conjugated polymers to generate semiconducting materials that are extremely insensitive to structural disorder.

TOC Graphics



All semiconducting polymers are formed by monomers containing a planar conjugated core connected with each other by a bond between sp2 hybridised atoms, typically carbon. The pi-conjugation can extend in principle for the length of the polymer chain. However, the highest-mobility polymers contain alkylic side chains to increase their solubility and form solid phases with no crystalline order. The conjugated core of the polymer chain is therefore non-planar and a distribution of torsional angles between the monomers is found. The disorder in the chain conformation causes localization of the orbitals and, according to essentially any model of transport in amorphous polymers, increasing disorder is associated with decreased mobility. To explain the high mobility observed in polymers lacking any long-range order it was proposed that they could possess some sort of short-range ordering due to aggregation.[1-2] Several independent studies have put forward the idea of tolerance[3] or resilience[4] to disorder, i.e. different mechanisms by which the amount of structural disorder in polymeric semiconductors is lower than expected, e.g. because of structural or electronic reasons.[5] Here we propose a strategy to design monomers such that the pi-conjugation is not broken by any level of disorder commonly encountered in polymers. We show that the electronic coupling between neighbouring monomers can be completely insensitive to torsions up to 60°. We provide a few examples to illustrate how this property can be easily built in, but, at the same time, it is unlikely to be present by chance.

Beside the property of having the right energy levels and band-gap there are very few guiding principles for the synthesis of completely new polymeric semiconductors. A survey of the literature[6-8] reveals few designs that have been more successful (e.g. donor-acceptor copolymers) and some monomers that feature more frequently in the highest charge mobility polymers (e.g. thiophene). The best materials at each given time have been subject to intense scrutiny and led to a number of the rationalizations put forward to explain retrospectively their excellent properties. Such explanations are convincing and well supported by experimental and theoretical data[9] but do not lend themselves to an immediate design of completely new materials. For example, it seems now very likely that some high-mobility polymers are characterized by short-range aggregation,[10-13] but such property is virtually impossible to build in, if one is seeking a completely new chemistry. Similarly, the idea that even a disordered polymer can retain a relatively planar conjugate core[4] is attractive but it is very hard to design polymers with the right rigidity of the core and flexibility of the side chains to achieve high mobility and high solubility at the same time. Given the immense difficulty in predicting phase characteristics of polymers, the best hope to find new chemical design rules is to look at designing the interaction between monomers within the polymer chain.

It is expected that the electronic coupling between conjugated monomers is maximum when they lay in the same plane, i.e. the dihedral angle between the monomer planes θ is zero. If we consider p-type semiconductors, the electronic coupling is the transfer integral between the HOMO orbitals localized on each monomer. It is also expected that, as the angle θ is increased, the electronic coupling τ decreases as ~cos(θ). This stems from the properties of the p_z orbitals whose linear combination generates the monomers' HOMO and has been verified with advanced computational methods many times in the past.[14-15] For illustration, we show in Figure 1 that the expected ~cos(θ) dependence is very close to what is computed from electronic structure calculations (computational details are given at the end) for a fluorene dimer, labelled as (1) in the figure. Additional examples of this "standard" behaviour are given in the supporting information. The existence of a broad distribution of torsional angles around the equilibrium position is the main origin of electronic disorder,[16] charge localization and the presence of an activation energy for transport in polymers.[17]

The ideal polymer can be thought as the one such that the electronic coupling between its conjugated monomers is not affected by the torsional angle between them. This condition may

seem inconsistent with elementary chemistry but it is indeed possible to find conjugated monomers with this property. One of them, illustrated in Figure 1 and labelled as (2), is the dimer or diketopyrrolo-pyrrole (DPP) also featuring in a large class of semiconducting polymers.[18] A dimer of DPP has the property that the electronic coupling between the HOMOs localized on each monomer is completely insensitive to the torsional angle up to 60°. For homodimers (with inversion centre) the electronic coupling between the monomers' HOMOs is simply half the energy difference between the HOMO and HOMO-1 of the dimer and the insensitivity of the electronic coupling to the torsion al angle can be immediately seen from the constant energy difference between HOMO and HOMO-1 in the dimer as the torsional angle between them is changed (shown in Figure S3 in the SI). The equilibrium torsional angle for the dimer of DPP is 0° and the barrier for rotation is particularly high (~0.8 eV) because of hydrogen bonding between the monomers. The electronic structure of a hypothetical chain of DPP monomers is therefore almost completely insensitive to the conformation of the chain, unlike what happens with a typical polymer.

We have considered (see Figure 1) a number of dimers that preserve the same local chemical structure (connection between 5-membered rings with strong single-double bond alternation) the simpler of which is a dimer of cyclopentadiene (molecule (6) where few atoms have been labelled as **A**, **B**, **C**, **A'**, **B'**, **C'**). All molecules (2)-(6) have a similar nodal structure of the HOMO near the connection between the dimers, i.e. strong bonding character between the atoms formally double bonded **A**-**B** and strong antibonding character between the formal single bond **A**-**C**. All these molecules display, to a different degree, a deviation from the ~cos(θ) behaviour. Molecule (3) replicates the same local chemistry and behaves identically to molecule (2); molecule (4) displays a stronger inter-monomer coupling at larger angle with maximum close to ~40°. Molecule (5) isoelectronic to molecule (2) but with a different bonding pattern displays the same level of insensitivity to the torsional angle. The simplest molecule (6) shows a coupling pattern intermediate between the standard ~cos(θ) behaviour and the extremely low dependence on the torsional angle seen for (2), (3), (5). A potentially relevant feature is that the carbon-carbon bond between atoms **AA'** is outside the plane defined by the atoms **ABC** by 19.2°, 19.1°, 12.2°, 9.0°, 4.1° for molecule (2), (3), (4), (5), (6) at θ=60°.

To explain the observation we first noted that molecules (2) and (3) maintains a strong H-bond between the amide and carbonylic oxygen up to large torsional angles (e.g. the H-O distance in (2) is 2.27 and 2.44 Å at θ=45° and θ=60° respectively) and the structure appears to be substantially influenced by this type of interaction. However the H-bond is not the reason for the unusual inter-monomer coupling as demonstrated by the same behaviour seen in molecule (5) with no inter-monomer H-bond (the closest inter-monomer N-H distance at θ=45° and 60° is 2.65 and 3.14 Å respectively and the relevant H atom is not a good H-bond donor). As molecule (5) also displays the more modest out of plane deviation for the **AA'** bond it is probably the best model system to investigate the electronic origin of this phenomenon. Visually inspecting the HOMO and HOMO-1 orbitals at different torsional angles (see Figure 2 (top)) there is no apparent change in the nodal structure of the orbitals. Analysing quantitatively the orbital population on each atom the differences are too modest and with the wrong sign to account for the observation; for example the HOMO population on atom **A** decreases by 9% by increasing the torsion from θ=0° to θ=60° (while a substantial *increase* may have explained the observation in Fig. 1). Consistently with the data above, the bond distances within each monomer of (5) do not change by more than 0.010 Å in the 0-60° interval, while there is the expected increase of the central carbon-carbon bond from 1.446 to 1.464 Å as the torsional angle is increased in this interval due to the decrease of the double bond character.

If the local orbital structure on each fragment is not changing there should be a strong correlation between the coupling computed from the HOMO-HOMO-1 energy splitting and the overlap integral between orbitals localized on the two monomers. We have therefore computed the HOMO on the two separated fragments in the same relative orientation of the dimer (saturating the dangling bond with an H atom) and computed the overlap integrals between these localized HOMOs. We see (Figure 3) that the total overlap is also insensitive to the torsional angle up to 60°. From this test it is possible to rule out explanations based on orbital re-hybridization in the dimer: the effect is more simply related to a first order orbital overlap interaction. The overlap can be decomposed into pairwise atomic components and the figure illustrates how the components involving the atoms **ABC** and **A**'**B**'**C**' account for almost the totality of the overlap (and the behaviour of the coupling). The **AA**' coupling follows a cos(θ) dependence, but the other contributions (i) are not much smaller, (ii) do deviate from the cos(θ) dependence, and (iii) (more than) compensate for the decrease of the overlap in the θ=0-60° interval. In particular the **BC**'+**C**'**B** component becomes less negative as θ is increased becoming the main responsible for the non-cos(θ) behaviour observed. Even the deviation from ideal behaviour in molecule (6) can be explained in a similar fashion with the totality of the deviation being due to the **BC**'+**C**'**B** component, which is smaller for (6) because of the smaller orbital weight on atom **C** (note that the **AA**' coupling needs not to be small). The range of behaviours observed in molecules (2)-(6) depends on the detail of the electronic and geometric structure. In the SI we have verified that there is no direct relation between this behaviour and the out of plane angle of the **AA**' bond with respect to the molecular (**ABC** or **A**'**B**'**C**') plane.

Finally, it is natural to ask whether a monomer designed in such a way that the coupling with another identical monomer is insensitive to the intermolecular torsional potential can bring the same properties to a molecular chain formed by alternating monomers. The answer is affirmative. A model of copolymer containing two repeat units is shown in Figure 3 and represents a minimal model of the polymer reported in ref. [19] and displaying a mobility of 0.9 cm^2/Vs. The coupling between the repeat units as a function of two torsional angles is also reported in the figure (see the supporting information for the non-trivial evaluation of the coupling in this non-symmetric case). One can see that, again very unexpectedly, the intra-chain coupling does not follow the cos(θ) behaviour when the torsion around the angle θ_1, adjacent to the DPP unit, is considered. The intra-chain coupling is much less sensitive to changes of θ_1, e.g. distortions from planarity of 60° cause a decrease of the intra-chain coupling of ~15% rather than the expected 50%. The torsional barrier around θ_1 is ~0.25 eV, close to the value reported for common polymers,[4] implying that the high barriers seen for the dimers are not essential to see reduced angular dependence of the coupling. Conversely, if one considers the rotation around the other torsional angle θ_2 the expected ~cos(θ) behaviour is found. It is important to stress that insensitivity to torsional disorder is not a standard feature of high mobility polymers and, for this reason, it constitutes a new design principle rather than an explanation of the existing results. In Figure 4 we illustrate this point considering two models of high mobility isoindigo-based polymer discussed in refs.[4] and [20] respectively and referred to as IDTBT and IIDT in these works. The coupling along the chain displays the expected ~cos(θ) behaviour in these cases. The IDTBT polymer was shown in ref.[4] to display a low level of disorder due to its high level of conformational order along the conjugated chain, not to the insensitivity to the disorder. As discussed more extensively in [5] a reduced disorder can be either a geometric or an electronic feature with ref.[4] being an example of the former and the effect discussed in this paper of the latter. The two approaches are complementary and can be possibly combined in future designs.

One should bear in mind that the torsional angle distribution in bulk polymers is not the one that can be deduced by vacuum calculations on oligomers: some large deviation from the ideal conformation

are unavoidable when the solvent is removed from entangled polymers and a polymer chain should be resilient to substantial deviations from the lowest energy conformation. Still, to provide a rough idea of the effect of reduced disorder on mobility we can estimate the fluctuation of the inter-monomer coupling using a Boltzmann distribution for the torsional angle. As detailed in the SI, for typical torsional barriers of 10 k_BT, a cos(θ) dependence of the coupling is expected to provide a fluctuation of about 4 % (defined as standard deviation σ divided by average coupling $\overline{V}$). The fluctuation is less than 1% for molecules with reduced dependence on the angle like (2) or (5). A connection between static fluctuation of the coupling and charge mobility along a single chain is proposed in the model of ref. [21], which also includes the effect of nuclear relaxation around a charge carrier because of electron-phonon coupling terms. According to the model and for a range of electron-phonon coupling strengths, a change of the fluctuation from 1 to 4% decreases the mobility by almost two orders of magnitude in a homopolymer, but the exact effect could be influenced by other sources of disorder if the torsional disorder is almost completely suppressed (see the SI for an estimate of the effect in the co-polymer case).

We would like to stress that we fully acknowledge the importance of many other factors in determining the charge mobility of semiconducting polymers, some of them outlined in the introduction. The high importance we attach to the insensitivity of the inter-monomer coupling is that it can be truly designed and verified experimentally on small model systems,[22-23] while the contributions of electrostatic disorder, inter-chain interaction, aggregation, micro-crystallinity cannot be really factored in when new polymer constituents are explored. We have implied throughout that the orbital coupling between oligomers can be used to build full polymer orbitals. This is an assumption that has been tested in different contexts[24-26] and it is more likely true if the band-width of the valence band is smaller than the energy difference with lower energy band (i.e. if there is no band hybridization), a condition that is more easily satisfied for co-polymers.[27]

In conclusion, we suggested that it is possible to design polymers whose electronic structure is insensitive to the conformational disorder of the polymer chain. The examples where this effect has been identified are based on the connection between sp2 carbons in five-membered rings with a marked single-double bond alternation within the ring. Testing for a similar property in other monomers would be computationally very inexpensive.

Methods. Electronic structure calculations have been performed with a variety of density functional theories belonging to different families, a standard hybrid functional (B3LYP[28]), a hybrid meta-GGA functional from the Minnesota family (M06[29]) and a long range corrected functional (ωB97X[30]). The results in the main manuscript are those obtained with B3LYP and 6-31+G** basis set, to allow the easiest reproducibility; the results with other methods are reported in the SI. The results are very consistent across the methods and the key observations in this paper can be considered independent from the computational detail. Even the basis set seems to play a modest role, with similar results obtained with the smaller 3-21G* basis set (not reported). Calculations at a given torsional angle imply that we have constrained one dihedral and while all other degrees of freedom have been optimized. In the SI we tested the constraint of different dihedrals and we repeated the calculation for molecule (2) and (5) as they relax unconstrained along the minimum energy path from the transition state near 90° to the equilibrium angle. The results are unaffected by the choice of the constraint.

For dimers formed by identical fragments related to each other by an inversion centre the coupling between monomers can be evaluated as the half-difference between HOMO and HOMO-1 energy of the dimer. Orbital energy diagrams shown in the SI confirm that the mixing with lower orbital is

expected to be negligible. For the oligomer in Figure 3 (the two portions of the molecule are inequivalent) the coupling is computed via a diabatization procedure described in the SI.

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Supporting Information. Further computational data with different density functionals and different dimers. Effect of the choice of constraints on the results. Fluctuations of the inter-monomer coupling. Method for the computation of the coupling in non-symmetric geometries.

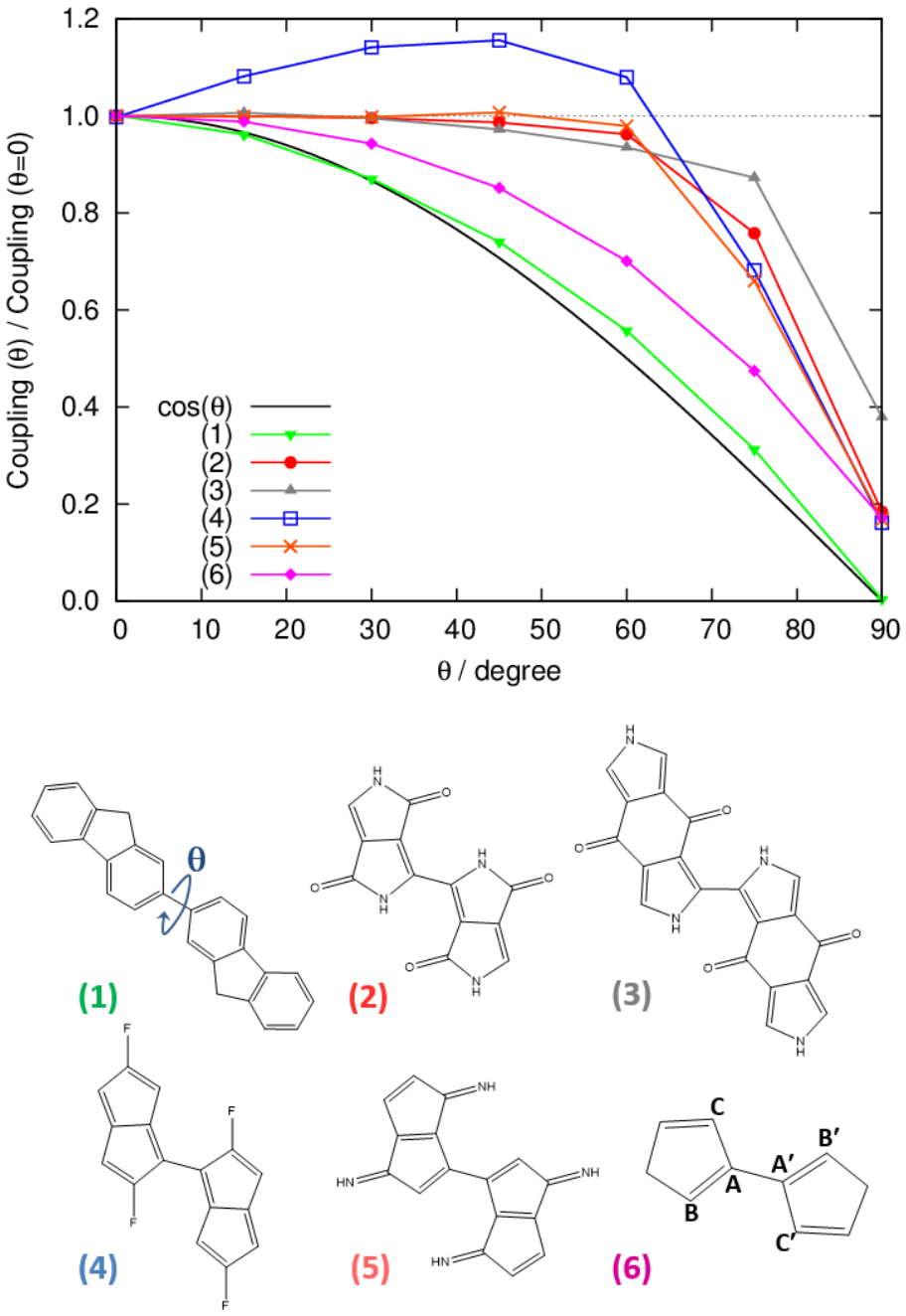

Figure 1. (bottom) Six dimers used to illustrate the expected (dimer **(1)**) and unexpected (dimers **(2)**-**(6)**) dependence of the inter-monomer electronic coupling on the torsional angle connecting the two. Dimer (6) illustrates the definition of atoms ABCA'B'C' used in the discussion. (top) The graph shows the electronic coupling between monomers as a function of θ relative to the value of the coupling at θ=0. The expected cosine dependence is also shown. The coupling at θ=0 is 457, 314, 459, 141, 175, 358 meV, respectively, for molecules **(1)**-**(6)**.

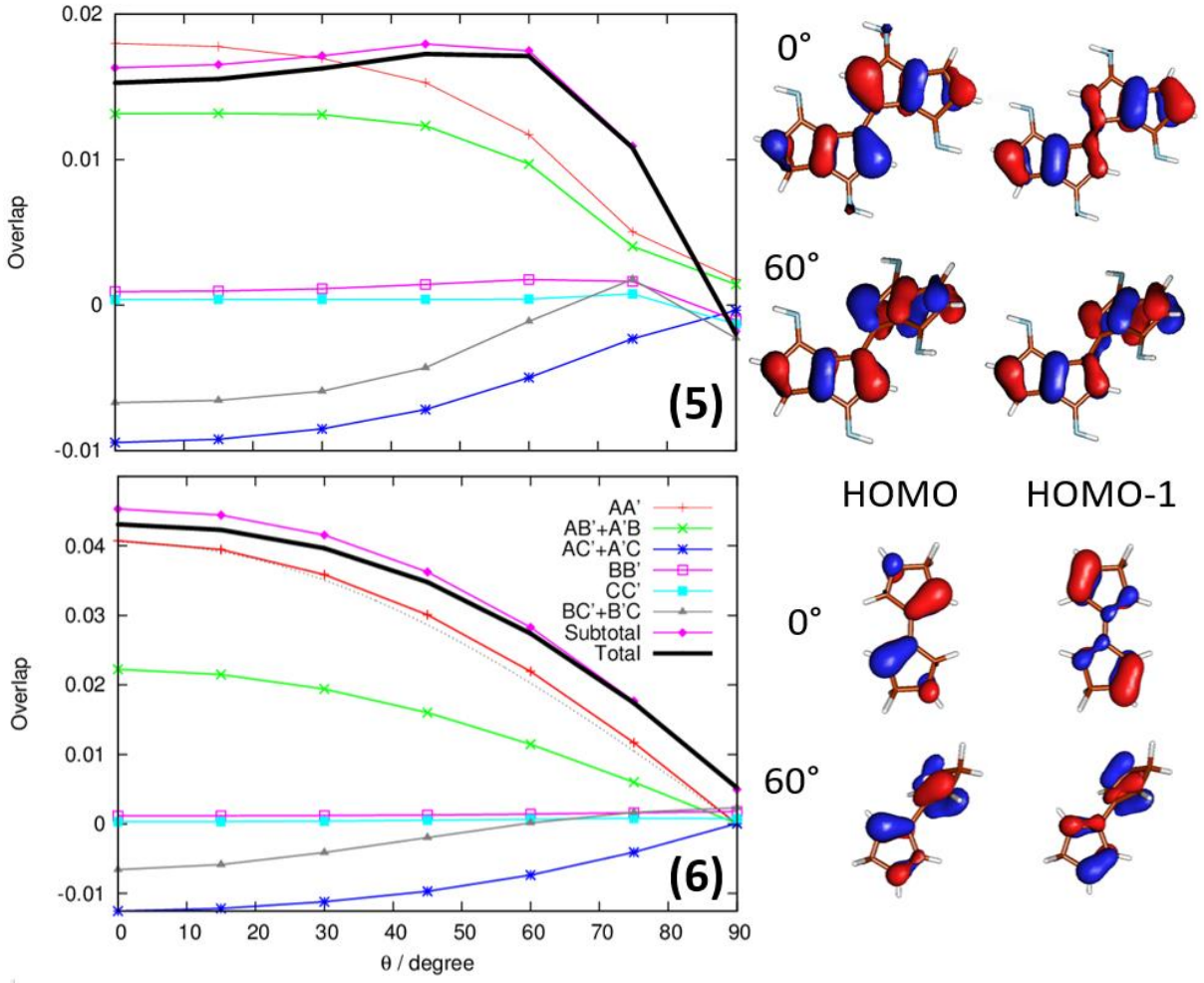

Figure 2. Overlap between HOMO orbitals localized on the two fragments of dimers (5) and (6). Thick black like is the total overlap, the other lines indicate the pairwise atomic contribution, e.g. the BC'+B'C line indicates all contributions from atomic orbital centered in atom BC' or B'C (see Figure 1 for the definition of these atoms). The subtotal line is the sum of all pairwise contributions represented in the figure. The atomic contributions to the overlap between atoms α and β are computed as $S_{\alpha\beta} = \sum_{i\ on\ \alpha} \sum_{j\ on\ \beta} C_i^{F1-HOMO} S_{ij} C_j^{F2-HOMO}$, where *i* and *j* are the atomic basis orbital index, S_{ij} is the overlap matrix of the dimer and $C_i^{F1(2)-HOMO}$ the coefficients of the HOMO on fragment 1(2).

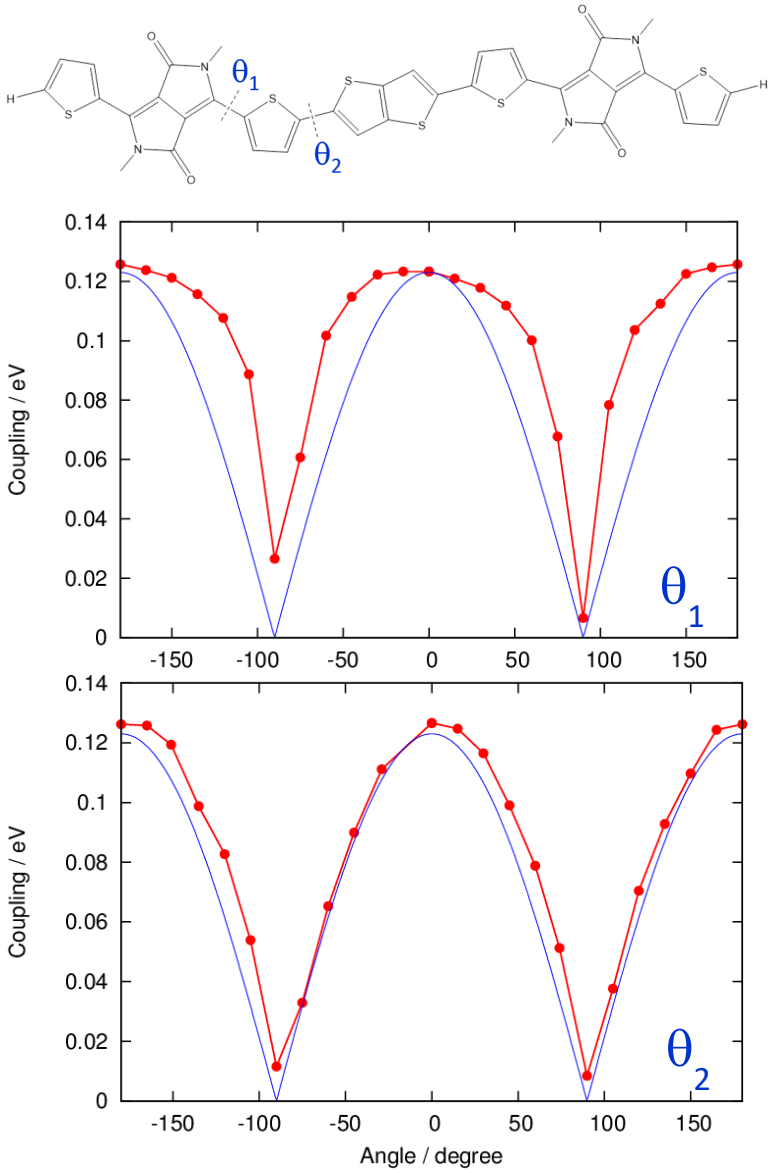

Figure 3. (top) An oligomer containing two DPP units with an indication of the two torsional angles that are rotated. (centre) Effective coupling between left and right fragments as a function of the torsional angle θ_1 (the solid blue line is a $A\cos(\theta)$ function for reference). (bottom) A similar plot for the rotation around angle θ_2. A strong deviation from the expected cosine dependence is seen only for the rotation θ_1.

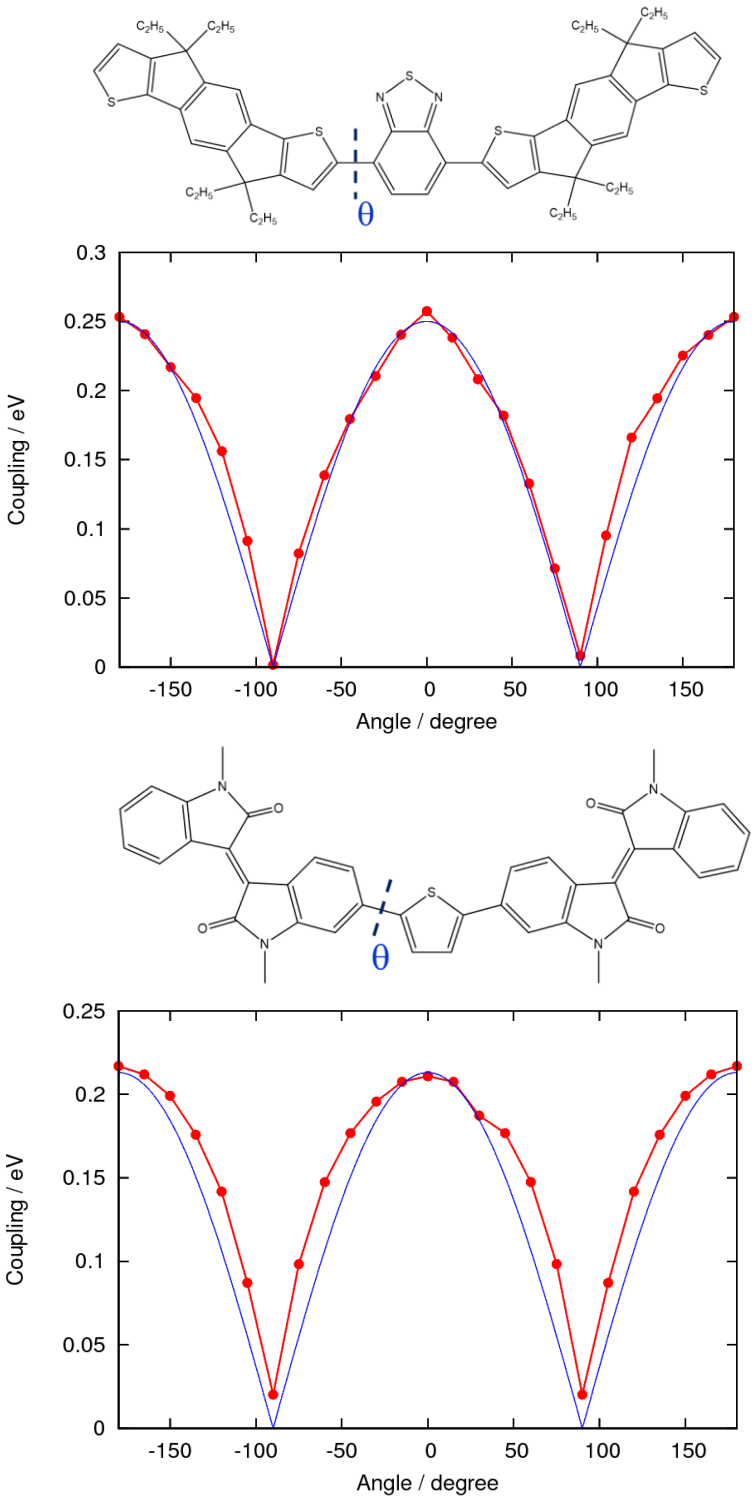

Figure 4. Chemical structure and effective coupling (red) between left and right fragments as a function of the torsional angle θ for two oligomers based on two high performing polymers (see text). In both cases the angular dependence is close to the expected $A\cos(\theta)$ function, shown in blue.

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